



PATENT SPECIFICATION

NO DRAWINGS

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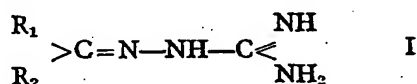
COMPLETE SPECIFICATION

Improvements in or relating to Guanidines

We, MAY & BAKER LIMITED, a British Company of Dagenham, Essex, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to new guanidine derivatives, to a process for their preparation, and to compositions containing them which are useful in the prevention and treatment of fungal diseases of plants.

It has been found that the alkylidene- and alkenylidene- amino guanidines of the general formula:

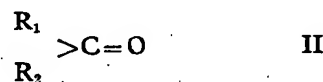


wherein R_1 represents an alkyl or alkenyl group containing five to seventeen carbon atoms, of which not more than thirteen are in a straight chain, and R_2 represents a hydrogen atom or a straight or branched alkyl group containing from one to five carbon atoms, and acid addition salts thereof, are active against fungi pathogenic to plants. These new compounds are, in consequence, particularly useful in the prevention and treatment of plant diseases caused by such fungi. Hence, they may be used as foliage protectants and seed dressings. In particular, they are active against brown rot in fruit (*Sclerotinea laxa*), scab in apples (*Venturia inaequalis*) and *Botrytis cinerea* infection of broad beans (similar to the Chocolate Spot infection (*Botrytis fabae*)).

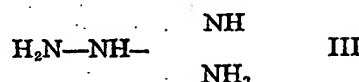
Preferred compounds according to the invention are those in which R_2 represents a hydrogen atom or a methyl group, and especially dodecylidene-aminoguanidine and 1-methyldodecylideneaminoguanidine and their acid addition salts.

According to the invention, the amino-
[Price 4s. 6d.]

guanidine derivatives of formula I are prepared by the reaction of a carbonyl compound of the formula:



(wherein R_1 and R_2 are as hereinbefore defined) with aminoguanidine of the formula:



or a salt thereof. The reaction is preferably effected using a solution or mixture of the carbonyl compound in water or a solvent such as ethanol, and an aqueous acid (or alkaline) solution of aminoguanidine. The aminoguanidine is preferably employed as a water-soluble acid addition salt.

When used as fungicides, the guanidine derivatives of formula I may conveniently be employed as their acid addition salts, it being understood that only such salts should in practice be employed as contain anions that are relatively innocuous to plants when used in effective doses so that the beneficial fungicidal properties inherent in the parent compound are not vitiated by injurious properties ascribable to those anions; in other words only non-phytotoxic salts are contemplated. Suitable acid addition salts include hydrohalides, for example, hydrochlorides, phosphates, nitrates, sulphates, borates and salts of organic acids, for example, acetates, succinates, and phthalates.

The invention is illustrated by the following Examples. The melting points given are uncorrected.

EXAMPLE I

Dodecanal (18.5 g.) in ethyl alcohol (100 ml.) was added dropwise with vigorous stirring to a solution obtained by dissolving amino-

guanidine bicarbonate (13.4 g.) in a slight excess of N nitric acid (ca. 105 ml.). The white solid which separated was collected and washed with water, ethyl alcohol and ether to give dodecylideneaminoguanidine nitrate, m.p. 84—86°C. A sample recrystallised from chloroform had a melting point of 95.0—95.5°C.

Similarly prepared from aminoguanidine nitrate and the appropriate carbonyl compound were the following:

- Heptylideneaminoguanidine nitrate, m.p. 84.5—85.5°C. (42% yield)
 1-methylheptylideneaminoguanidine nitrate, m.p. 103.5—104.5°C. (41% yield)
 15 Octylideneaminoguanidine nitrate, m.p. 86.5—87.5°C. (90% yield)
 Nonylideneaminoguanidine nitrate, m.p. 80—82°C. (80% yield)
 20 Decylideneaminoguanidine nitrate, m.p. 91.0—92.5°C. (42% yield)

Salts other than the nitrate can be made by replacing the nitric acid by the appropriate acid.

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EXAMPLE II

To a warm solution of aminoguanidine bicarbonate (17 g.) in 2N nitric acid (65 ml.) was added undec-10-enal (21.2 g.) in ethyl alcohol (50 ml.) and the mixture was mechanically shaken for 1 hour. The solid material thus obtained was washed with water, ethyl alcohol and ether and recrystallised from water (50 ml.), yielding undec-10-enylideneaminoguanidine nitrate, m.p. 84°C.

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EXAMPLE III

A solution of 5-formyl-2,2,4,8,10,10-hexamethylundec-5-ene (77 g.) in ethanol (200 ml.) was added to a solution of aminoguanidine nitrate (40 g.) in hot water (100 ml.) containing about 5 ml. of 2NHNO₃, and the mixture heated under reflux for 3 hours. The mixture was cooled and filtered. Trituration of the solid product, first with water (100 ml.), and then with ethanol (100 ml.), and then with ether (200 ml.) gave 2,2,4,8,10,10-hexamethylundec-5-ene-5-methyleneaminoguanidine nitrate (62 g.), m.p. 177—178°C.

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EXAMPLE IV

Aminoguanidine bicarbonate (40 g.) was dissolved in 2N nitric acid (160 ml.) and the solution added to 1-tetradecanal (63 g.) in ethanol (100 ml.). After shaking to permit mixing, the mixture was allowed to stand for 2 hours and then filtered. The solid product obtained was triturated with water (100 ml.), ethanol (100 ml.), and ether (100 ml.) and dried. After recrystallisation from ethanol (250 ml.), tetradecylideneaminoguanidine nitrate (60 g.), m.p. 83—84°C. was obtained.

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EXAMPLE V

Aminoguanidine bicarbonate (20 g.) was dissolved in 2N nitric acid (80 ml.) and the solution added to n-hexanal (14.7 g.) in ethanol (50 ml.). The mixture was mechanically shaken for 2 hours and then filtered. The crude product thus obtained was washed with a little water, ethanol and then ether, and recrystallised from ethanol. n-Hexylideneaminoguanidine nitrate (20 g.), m.p. 118—120°C., was thus obtained.

EXAMPLE VI

Aminoguanidine bicarbonate (5 g.) was dissolved in 2N nitric acid (20 ml.) by stirring until the reaction ceased and then warming to 40°C. Methyl nonyl ketone (6.25 g.) in ethanol (10 ml.) and water (10 ml.) was added, and the mixture shaken mechanically for 3 hours. The solid which separated was collected and recrystallised from water to give 1-methyl-decylideneaminoguanidine nitrate (6.5 g.), m.p. 85—86°C.

The present invention includes within its scope fungicidal compositions comprising one or more aminoguanidines of formula I, or an acid addition salt thereof, in association with one or more solid or liquid diluents of the types commonly used in fungicidal compositions. Such compositions may take the form of dusts, dispersions and emulsions. In the said compositions, there may also be incorporated one or more substances known to be active as fungicides, insecticides, bactericides, fertilisers or plant-growth regulating agents.

Examples of typical fungicidal compositions according to the invention are:

(a) Wettable powders comprising the active material dispersed in a concentration of, for example, up to 70% w/w in an inert absorbent carrier such as a siliceous earth together with an ionic or non-ionic wetting and/or dispersing agent such as an alkali metal salt of a long chain aliphatic sulphate, a partly neutralised sulphuric acid derivative of a petroleum oil or of naturally occurring glycerides or a condensation product of an alkylene oxide with an organic acid.

(b) Self-emulsifying concentrates comprising the active material in solution or suspension in a concentration of, for example, up to 80% w/v in a suitable solvent such as an aromatic hydrocarbon (e.g. xylene), solvent naphtha or a mineral oil together with an ionic or non-ionic wetting and/or dispersing agent.

(c) Dusts obtained by dispersing the active material in sufficient inert absorbent carrier to form a free-flowing powder and diluting the powder with one or more inert carriers such as talc, diatomaceous earths, woodflours and clays.

(d) Compositions of the active material formulated in the manner commonly employed for the preparation of fungicidal smokes, dusts and aerosols.

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100

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The concentrated compositions described under (a) and (b) yield, on dilution with water until the concentration of the active material is, for example, from 0.05% to 0.4% w/v, stable suspensions and emulsions respectively which may be used in the form of a spray.

The products of the present invention are, as already stated, particularly useful in the prevention and treatment of diseases of plants. They also have possible utility against fungi which attack cellulosic materials including textiles and leather, and the compositions of the present invention are also useful for treating such materials to prevent or minimise fungal attack.

The fungicidal properties of the compounds

of the invention are demonstrated by the following experimental results showing the inhibition of spore germination produced by the compounds of the invention.

The compounds were suspended or dissolved in aqueous mixtures containing 0.05% of a wetting agent at concentrations of 0.08, 0.8, and 8.0 ppm. The following tables gives the minimum concentration of active substance capable of inhibiting by 50±10% the germination of the named spores. In the table, a minimum concentration of 0.08 ppm. is indicated by 5, of 0.8 ppm. by 4, and of 8.0 ppm. by 3. The organisms tested were *Botrytis cinerea* (B.c.), (*Sclerotinia laxa*) (S.L.), and (*Venturia inaequalis*) (V.i.).

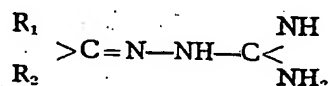
TABLE

Compound	Test Result		
	B.c.	S.L.	V.i.
Ethylideneaminoguanidine nitrate	o	o	o
Propylideneaminoguanidine nitrate	L	L	L
Butylideneaminoguanidine nitrate	L	L	L
Hexylideneaminoguanidine nitrate	3	3	3
Heptylideneaminoguanidine nitrate	3	3	4
1-Methylheptylideneaminoguanidine nitrate	3	3	4
Octylideneaminoguanidine nitrate	4	3	4
1-Methyldecylideneaminoguanidine nitrate	5	5	5
Dedecylideneaminoguanidine nitrate	4	4	5
Undecyl-10-enidineaminoguanidine nitrate	3	3	3
Tetradecylideneaminoguanidine nitrate	3	3	3
1-Methylpentadecylideneaminoguanidine nitrate	L	L	L
2,2,4,8,10,10-Hexamethylundec-5-ene-5-methyleneaminoguanidine nitrate	3	3	3
Nonylideneaminoguanidine nitrate	3	3	3
Decylideneaminoguanidine nitrate	3	3	3

In the Table L indicates that the compound showed a slight inhibitory activity at 8.0 ppm. while o indicates inactivity at this concentration. The first three and the twelfth compounds of the Table are not within the scope of the present invention.

WHAT WE CLAIM IS:—

1. Alkylidene- and alkenylidene- amino-guanidines of the formula:



and their acid addition salts, wherein R₁ represents an alkyl or alkenyl group containing 5 to 17 carbon atoms, of which not more than 13 carbon atoms are in a straight chain, and R₂ represents a hydrogen atom or a straight or branched chain alkyl group containing 1 to 5 carbon atoms.

2. Aminoguanidine derivatives as claimed in claim 1 in which R_2 is a hydrogen atom or a methyl group.
3. Dodecylideneaminoguanidine and its acid addition salts.
4. 1-Methyldodecylideneaminoguanidine and its acid addition salts.
5. Process for the preparation of the aminoguanidine derivatives claimed in claim 1 which comprises reacting aminoguanidine, or an acid addition salt thereof, with a carbonyl compound of the formula $R_1CO.R_2$, where R_1 and R_2 as defined in claim 1.
6. Process according to claim 5 in which the carbonyl compound is reacted with a water-soluble acid addition salt of aminoguanidine in an aqueous medium.
7. Process according to claim 5 substantially as described in any of Examples I to VI.
8. Alkylidene- and alkenylidene- aminoguanidines as claimed in claim 1 when prepared by the process claimed in any of claims 5 to 7.
9. A fungicidal composition comprising one or more aminoguanidine derivatives as defined in any of claims 1 to 4 and 8 in association with a solid or liquid diluent of the type commonly used in fungicidal compositions.
10. A fungicidal composition as claimed in claim 9 substantially as hereinbefore described.

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